Synthesis, Structure and Reactivity of O-Donor Ir(III) Complexes: C-H Activation Studies with Benzene

*Gaurav Bhalla, Xiang Yang Liu, Jonas Oxgaard,† William A. Goddard, III,† Roy A. Periana**

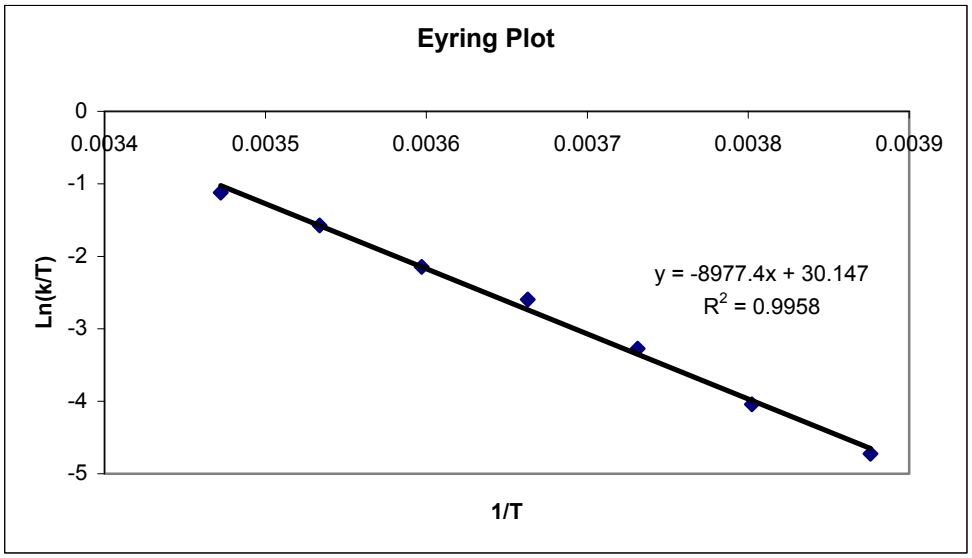
Loker Hydrocarbon Research Institute, Chemistry Department, University of Southern California, Los Angeles, California 90089-1661

† Materials and Process Simulation Center, Beckman Institute (139-74), Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California 91125

Table S1. Line-Broadening Analysis.

The mononuclear-dinuclear equilibrium was measured in the slow exchange region from the width of the NMR signals at half height using eq: $1/\tau_a = \pi(\omega_A - \omega^\circ_A)$ where τ_a is the residence time in site A and ω_A and ω°_A are the linewidths in the presence and in the absence of exchange, respectively. ω°_A was measured at a temperature where molecule was non exchanging in the NMR time scale. The experimental line widths were corrected by subtracting the line width of TMS to minimize the effect of instrumental line-broadening.

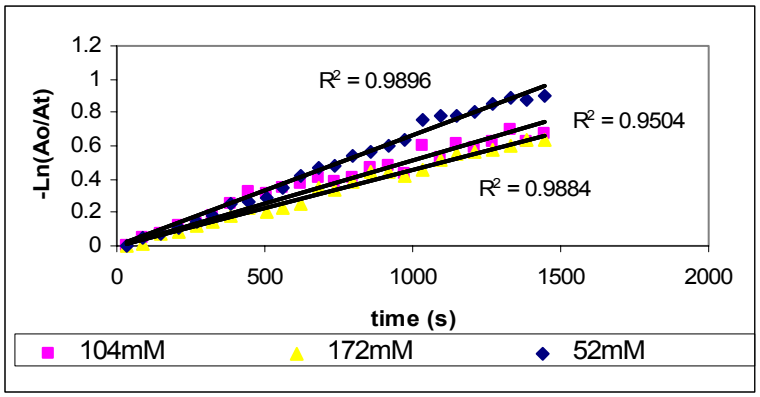
T / K	$(\omega_A - \omega^\circ_A)$ /Hz	K_{obs} / s^{-1}
253	0	0
258	0.73	2.29
263	1.47	4.62
268	3.23	10.2
273	6.48	20.4
278	10.36	32.56
283	18.66	58.65
288	29.91	94.00



$\Delta H^{\ddagger}$ = 17.8 ± 1 kcal/mol,
$\Delta S^{\ddagger}$ = 12.7 ± 2 eu,
$\Delta G^{\ddagger}$ (T=298K) = 14.1 ± 0.5 kcal/mol

Table S2. Py exchange with Ph-Ir-Py in $CDCl_3$ @276K.

	10eq (52mM)		20eq (104mM)		33eq (172mM)	
time (s)	**At**	**-Ln(Ao/At)**	**At**	**-Ln(Ao/At)**	**At**	**-Ln(Ao/At)**
31.96	85	0	65	0	82	0
90.92	89	0.045985113	68	0.04512	83	0.012121361
149.9	91	0.06820825	70	0.074108	87.8	0.068342253
208.8	95	0.111225635	72.9	0.114701	89.5	0.087519378
267.8	98	0.142316222	74	0.129678	92	0.11506933
326.7	102	0.182321557	78	0.182322	95	0.147157644
385.7	110	0.257829109	83.2	0.24686	98	0.178248231
444.7	111	0.266878945	89.8	0.323198	103	0.228009741
503.6	113	0.284736562	89.2	0.316494	101	0.20840127
562.6	121	0.353139289	92	0.347401	103	0.228009741
621.5	130	0.424883194	94.8	0.377382	106	0.256719847
680.5	135	0.462623522	98	0.41058	116	0.346870944
739.5	138	0.484602429	95.1	0.380542	115	0.338212881
798.4	145	0.534082486	98.3	0.413637	120	0.380772496
857.4	150	0.567984038	104	0.470004	128	0.445311017
916.3	155	0.60077386	105	0.479573	128	0.445311017
975.3	160	0.632522559	100	0.430783	125	0.42159449
1034	181	0.755845775	118	0.596297	130	0.460815203
1093	185	0.777704569	110	0.526093	137	0.513261679
1152	185	0.777704569	120	0.613104	143	0.556125383
1211	190	0.804372816	117	0.587787	144	0.563094052
1270	200	0.85566611	122	0.629634	146	0.576887374
1329	206	0.885224912	130	0.693147	149	0.597227059
1388	205	0.880358723	122	0.629634	155	0.63670587
1447	209	0.899682995	127	0.6698	155	0.63670587



Plot of k_{obs} vs [Py]

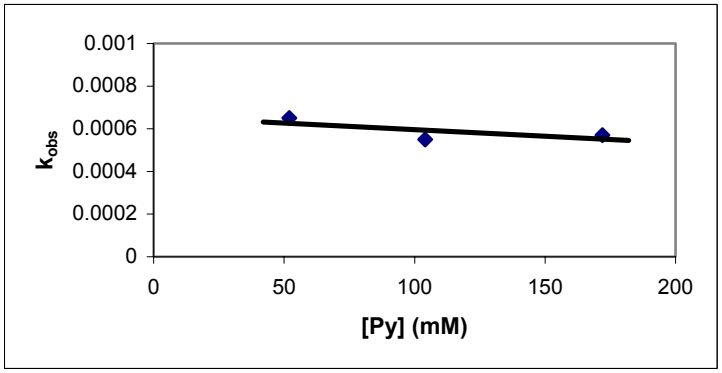
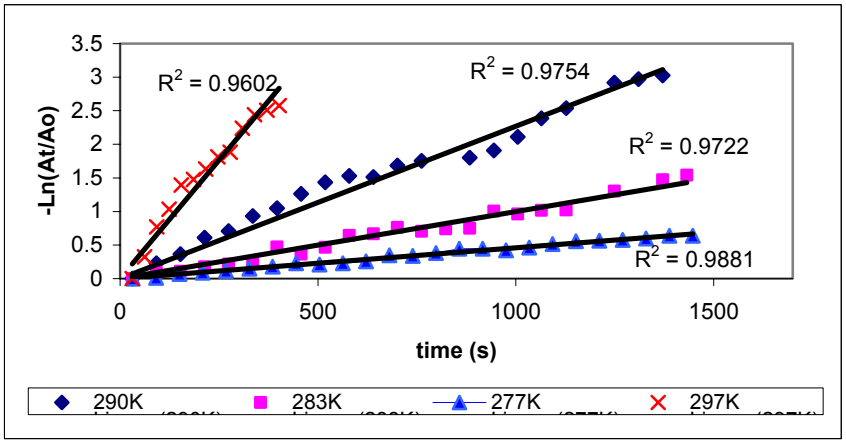
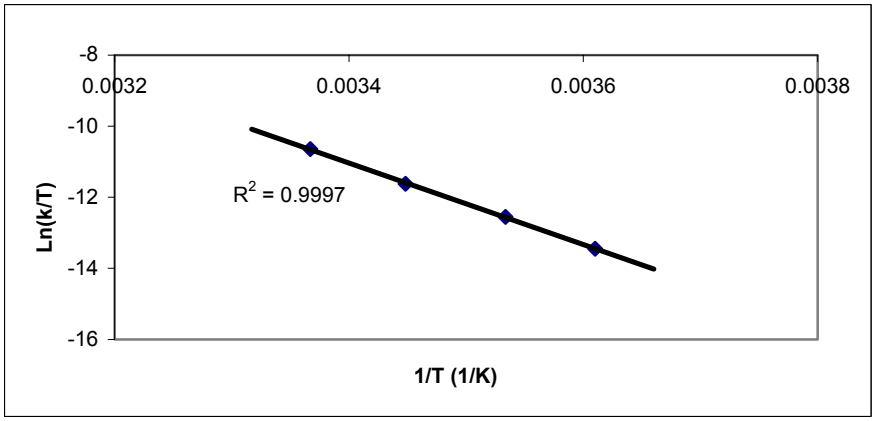


Table S3. Eyring Plot for Pyridine Exchange with Ph-Ir-Py.

	290 K		283 K		297K		
time (s)	At	-Ln(At/Ao)	At	-Ln(At/Ao)	time	At	-Ln(At/Ao)
30.91	37.1	0	64.5	0	30.91	92	0
91.82	29.5	0.229226706	58.9	0.090824	61.82	66.5	0.324586629
152.7	25.8	0.363242478	57.8	0.109676	92.73	42.6	0.769934324
213.6	20.2	0.607934365	54.1	0.175831	123.6	32.7	1.034413499
274.5	18.3	0.70671591	52	0.215422	154.6	22.8	1.395028041
335.5	14.6	0.932595441	50.4	0.246674	185.5	21	1.477266139
396.4	13	1.048667612	40.3	0.470314	216.4	18	1.631416819
457.3	10.5	1.262241712	44.8	0.364457	247.3	15	1.813738376
518.2	8.84	1.434330093	40.5	0.465363	278.2	14	1.882731247
579.1	8.03	1.530432442	33.9	0.64325	309.1	9.8	2.239406191
640	8.17	1.513148061	33.1	0.667132	340	8	2.442347035
700.9	6.88	1.684998318	30.1	0.76214	370.9	7.5	2.506885557
761.8	6.43	1.752642431	31.9	0.704059	401.8	7	2.575878428
822.7	4.74		30.8	0.739151			
883.6	6.12	1.802054873	30.5	0.748939			
944.6	5.5	1.908868877	23.6	1.005419			
1005	4.5	2.109539573	24.6	0.963919			
1065	3.41	2.386904678	23.3	1.018212			
1127	2.93	2.538614547	23.2	1.022513			
1188	3.05		16				
1249	2	2.920469789	17.5	1.304464			
1310	1.9	2.971763083	21.4				
1371	1.8	3.025830305	14.8	1.472038			
1432			13.8	1.541997			



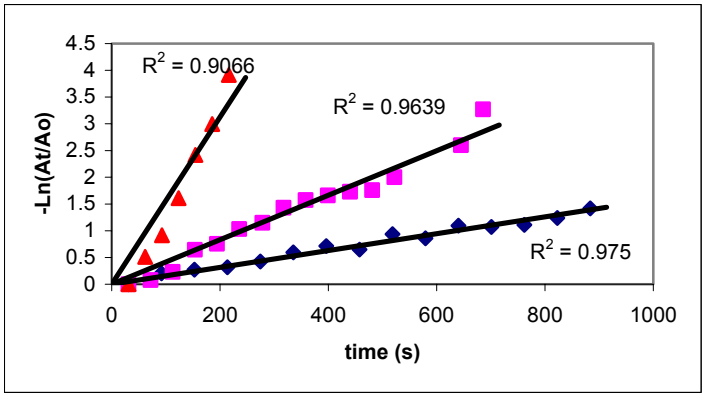
T (K)	1/T	kobs	Ln(K/T)
277	0.00361	0.0004	-13.448064
283	0.003534	0.001	-12.553202
290	0.003448	0.0026	-11.622125
297	0.003367	0.0071	-10.641393



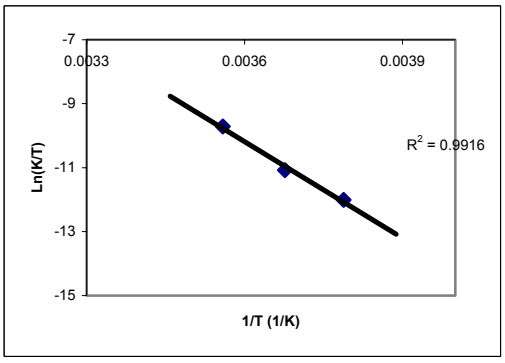
$\Delta H^{\ddagger} = 22.8 \pm 0.5$ kcal/mol,
$\Delta S^{\ddagger} = 8.4 \pm 1.6$ eu,
$\Delta G^{\ddagger}$ (T=298K) = 20.3 ± 0.5 kcal/mol

Table S4. Eyring Plot for Pyridine Exchange for CH_3-Ir-Py.

264K			272K			281K		
time (s)	At	-Ln(At/Ao)	time (s)	At	-Ln(At/Ao)	time (s)	At	-Ln(At/Ao)
30.91	38	0	30.91	79	0	30.91	10	0
91.82	31	0.203599	71.82	73	0.078988	61.82	6	0.510826
152.7	29	0.27029	112.7	62.8	0.229493	92.73	4	0.916291
213.6	27.7	0.316154	153.6	41.4	0.646167	123.6	2	1.609438
274.5	24.9	0.422718	194.5	37.1	0.755831	154.5	0.89	2.419119
335.5	21	0.593064	235.5	28.1	1.033678	185.5	0.5	2.995732
396.4	18.6	0.714425	278.4	25	1.150572	216.4	0.2	3.912023
457.3	19.9	0.646866	317.3	18.9	1.430286			
518.2	14.9	0.936225	358.2	16.4	1.572167			
579.1	16.1	0.858767	399.1	15	1.661398			
640	12.7	1.095984	440	14	1.730391			
700.9	13	1.072637	480.9	13.6	1.759378			
761.8	12.5	1.111858	521.8	10.7	1.999204			
822.7	11	1.239691	562.7					
883.6	9.21	1.417296	603.6					
			644.7	5.87	2.599593			
			685.5	3	3.270836			



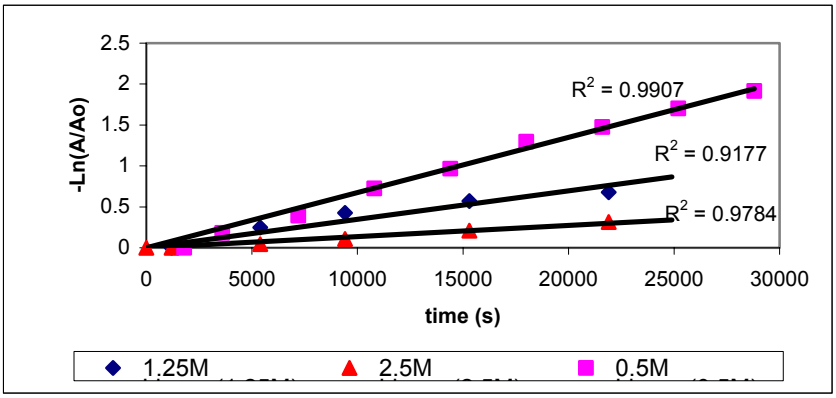
T (K)	1/T	kobs	Ln(k/T)
264	0.003788	0.0016	-12.0137
272	0.003676	0.0042	-11.07847
281	0.003559	0.017	-9.712897



$\Delta H^{\ddagger} = 19.9 \pm 1.4$ kcal/mol,
$\Delta S^{\ddagger} = 4.4 \pm 5.5$ eu,
$\Delta G^{\ddagger}$ (T=298K) $= 18.6 \pm 0.5$ kcal/mol

Table S5. Ligand Effect on Trans-Cis Isomerization with Ph-Ir-Py.

0.5M		1.25 M		2.5 M	
Time (s)	-Ln(At/Ao)	Time (s)	-Ln(At/Ao)	Time (s)	-Ln(At/Ao)
0		0		0	0
1800	0	1200	0.000	1200	0
3600	0.184086	5400	0.250	5400	0.044742
7200	0.394168	9420	0.427	9420	0.110169
10800	0.724862	15300	0.571	15300	0.211548
14400	0.967679	21900	0.679	21900	0.31659
18000	1.29755				
21600	1.475528				
25200	1.701462				
28800	1.914759				



[Py]	1/[Py]	kobs	kobs x 10-5
0.5	2	0.000044	4.4
1.25	0.8	0.00003	2.8
2.5	0.4	0.000014	1.3

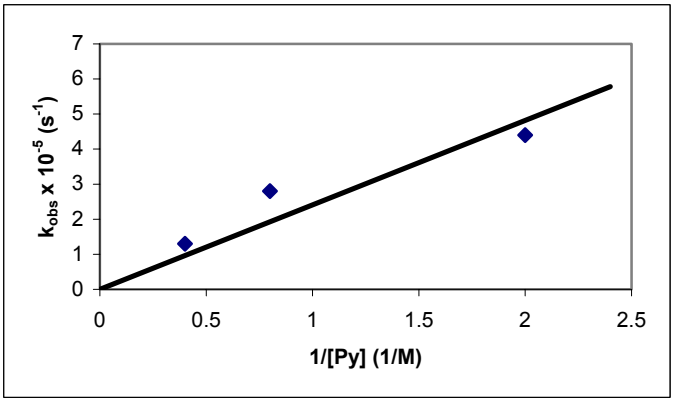
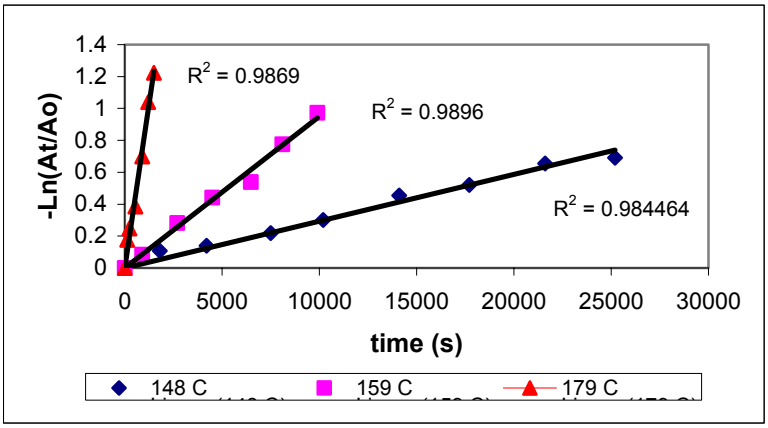
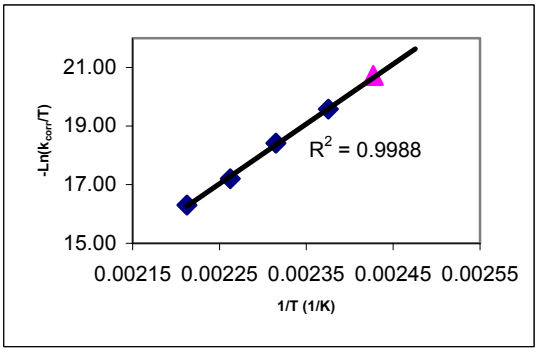


Table S6. Eyring Plot for CH Activation of C_6D_6 with CH_3-Ir-Py @ constant $[Py]/[C_6D_6] = 0.045$

148 C		159 C		179 C	
time (s)	-Ln(At/Ao)	time (s)	-Ln(At/Ao)	time (s)	-Ln(At/Ao)
0	0	0	0	0	0
1800	0.107496	900	0.082972	120	0.176654
4200	0.139367	2700	0.281758	240	0.247311
7500	0.217868	4500	0.442112	540	0.384734
10200	0.300359	6480	0.538559	900	0.699193
14100	0.454189	8100	0.775522	1200	1.039833
17700	0.520686	9900	0.972099	1500	1.22385
21600	0.654717				
25200	0.690989				



Temp C	Temp (K)	1/T	kobs	kobs x Py/[Bz] (s^{-1})	[-LN(kcorr/T)]
179	452	0.002212	0.000823	3.74759E-05	16.31
169	442	0.002262	0.000329	1.49816E-05	17.20
159	432	0.002315	0.000095	4.32589E-06	18.42
148	421	0.002375	0.000029	1.32054E-06	19.58
139	412	0.002427	0.000009	4.09821E-07	20.73

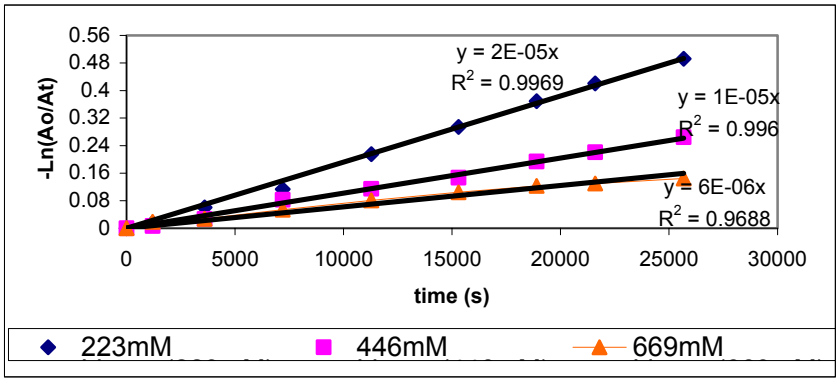


Eyring Plot for the reaction of **CH_3-Ir-Py (◆)** with C_6D_6 at $[Py]/[C_6D_6] = 0.045$. $k_{corr} = k_{obs}$ x $[Py]/[C_6D_6]$.
▲ = **$PhCH_2CH_2$-Ir-Py**.
$\Delta H^{\ddagger} = 41.1 \pm 1.1$ kcal/mol,
$\Delta S^{\ddagger} = 11.5 \pm 3.0$ eu,
$\Delta G^{\ddagger}$ (T=298K) $= 37.7 \pm 1.0$ kcal/mol

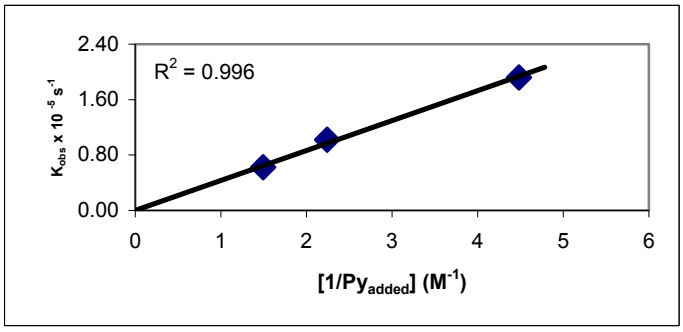
Table S7. L Dependence on CH Activation of Benzene with $PhCH_2CH_2$-Ir-Py at 140 °C.

15eq (223mM)			30 eq (446mM)			45 eq (669mM)		
Time (s)	At/Ao	-Ln(At/Ao)	Time (s)	At/Ao	-Ln(At/Ao)	Time (s)	At/Ao	-Ln(At/Ao)
0	1.00	0.000	0	1.00	0.000	0	1.00	0.000
1200	0.98	0.015	1200	0.99	0.007	1200	0.98	0.019
3600	0.94	0.060	3600	0.97	0.027	3600	0.97	0.027
7200	0.89	0.113	7200	0.92	0.083	7200	0.95	0.054
11280	0.81	0.215	11280	0.89	0.115	11280	0.92	0.081
15300	0.74	0.294	15300	0.86	0.147	15300	0.90	0.105
18900	0.69	0.369	18900	0.82	0.194	18900	0.88	0.123
21600	0.66	0.421	21600	0.80	0.221	21600	0.88	0.130
25680	0.61	0.492	25680	0.77	0.265	25680	0.87	0.145

First order plots for Py_{added} for C-H activation of **$PhCH_2CH_2$-Ir-Py** at 140 °C



[Py] (M)	1/Py	Kobs x10-5 (s-1)
0.223076923	4.482758621	1.92
0.446153846	2.24137931	1.02
0.669230769	1.494252874	0.62



S8. Benzene Dependence on CH Activation using Cy-Ir-Py

5600mM

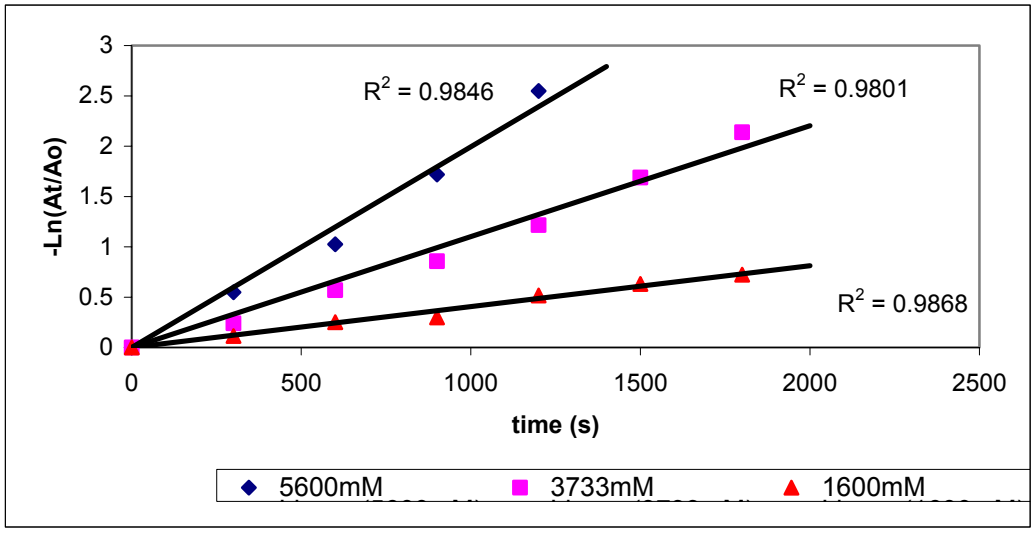
Time (s)	At/Ao	-Ln(At/Ao)
0	78.13	0
300	45.1	0.549492
600	28	1.02617
900	14	1.719317
1200	6.11	2.548447

3733mM

Time (s)	At/Ao	-Ln(At/Ao)
0	63.61	0
300	50	0.240748
600	36	0.569252
900	27	0.856934
1200	18.87	1.215197
1500	11.75	1.688917
1800	7.5	2.137868

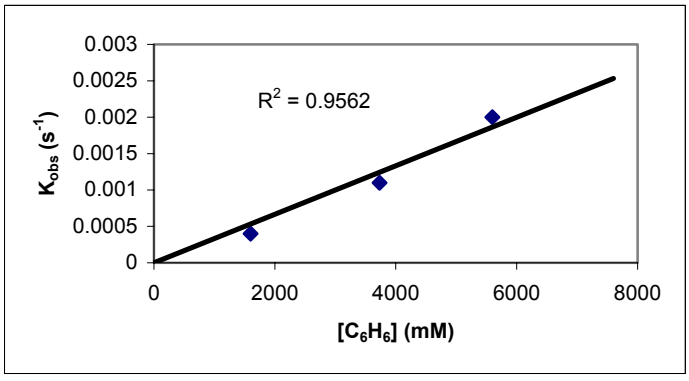
1600mM

Time (s)	At/Ao	-Ln(At/Ao)
0	128.93	0
300	115	0.114337
600	100.22	0.251902
900	95.45	0.300667
1200	76.87	0.517154
1500	68.59	0.631123
1800	62.53	0.723623



A plot of K_{obs} vs $[C_6H_6]$ at 120 °C with **Cy-d_{11}-Ir-Py**

$[C_6H_6]$ (mM)	kobs (s^{-1})
5600	0.002
3733	0.0011
1600	0.0004



X-ray diffraction data were collected on a Bruker SMART APEX CCD diffractometer with graphite monochromated Mo-Kα radiation (λ = 0.71073 Å). The cell parameters were obtained from the least-squares refinement of the spots (from 60 collected frames) using the program SMART. A hemisphere of data was collected up to a resolution of 0.75Å. The intensity data were processed using the program Saint-Plus. All calculations for the structure determination were carried out using the SHELXTL package (version 5.1). Initial atomic coordinates of the Ir atoms were located by direct methods, and structures were refined by least-squares methods. Empirical absorption corrections were applied using the program SADABS. Calculated hydrogen positions were input and refined in a riding manner along with their attached carbons. A summary of the refinement details and the resulting parameters are given in supporting information.
The crystal structure of the **Ph-Ir-Py** is disordered. As a result, the molecule lies on a center of symmetry necessarily causing the phenyl group or the pyridine group to be disordered.

Table 1. Crystal data and structure refinement for acacm.(**Ph-Ir-Py**)

Identification code	acacm	
Empirical formula	C21 H24 Ir N O4	
Formula weight	546.61	
Temperature	298(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 8.1041(9) Å	α= 90°.
	b = 9.6690(10) Å	β= 94.113(2)°.
	c = 13.2092(14) Å	γ = 90°.
Volume	1032.39(19) $Å^3$	
Z	2	
Density (calculated)	1.758 Mg/m^3	
Absorption coefficient	6.491 mm^{-1}	
F(000)	532	
Crystal size	0.94 x 0.57 x 0.494 mm^3	
Theta range for data collection	2.61 to 27.52°.	
Index ranges	-10<=h<=9, -11<=k<=12, -15<=l<=16	
Reflections collected	6140	
Independent reflections	2266 [R(int) = 0.0312]	
Completeness to theta = 27.52°	95.0 %	
Transmission factors	min/max ratio: 0.629	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2266 / 0 / 126	
Goodness-of-fit on F^2	1.261	
Final R indices [I>2sigma(I)]	R1 = 0.0407, wR2 = 0.0900	

R indices (all data)	R1 = 0.0467, wR2 = 0.0926
Largest diff. peak and hole	1.323 and -0.949 e.Å^{-3}

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for acacm. (**Ph-Ir-Py**) U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Ir(1)	0	5000	5000	35(1)
O(2)	847(6)	4631(4)	3622(3)	37(1)
O(1)	1945(5)	6167(5)	5515(3)	36(1)
N(1)	1195(7)	3205(6)	5573(4)	37(1)
C(1)	4487(9)	7288(8)	5472(7)	53(2)
C(2)	3132(8)	6412(7)	4977(6)	40(2)
C(3)	3302(9)	5963(8)	3992(6)	49(2)
C(4)	2213(9)	5156(7)	3380(5)	43(2)
C(5)	2629(13)	4741(10)	2318(6)	69(3)
C(6)	1195(7)	3205(6)	5573(4)	37(1)
C(7)	1117(9)	1983(8)	5047(6)	46(2)
C(8)	1883(10)	802(8)	5420(7)	54(2)
C(9)	2764(11)	817(9)	6333(7)	60(2)
C(10)	2851(11)	2040(10)	6888(6)	61(2)
C(11)	2078(10)	3220(8)	6495(5)	48(2)

Table 3. Bond lengths [Å] and angles [°] for acacm. (**Ph-Ir-Py**)

Ir(1)-O(1)#1	2.016(4)
Ir(1)-O(1)	2.016(4)
Ir(1)-O(2)	2.022(4)
Ir(1)-O(2)#1	2.022(4)
Ir(1)-C(6)#1	2.102(6)
Ir(1)-N(1)#1	2.102(6)
Ir(1)-N(1)	2.102(6)
O(2)-C(4)	1.279(9)
O(1)-C(2)	1.259(8)

N(1)-C(11)	1.367(9)
N(1)-C(7)	1.370(9)
C(1)-C(2)	1.499(9)
C(2)-C(3)	1.389(10)
C(3)-C(4)	1.392(10)
C(4)-C(5)	1.520(10)
C(7)-C(8)	1.375(10)
C(8)-C(9)	1.357(12)
C(9)-C(10)	1.390(12)
C(10)-C(11)	1.385(11)

O(1)#1-Ir(1)-O(1)	179.999(1)
O(1)#1-Ir(1)-O(2)	84.56(18)
O(1)-Ir(1)-O(2)	95.44(18)
O(1)#1-Ir(1)-O(2)#1	95.44(18)
O(1)-Ir(1)-O(2)#1	84.56(18)
O(2)-Ir(1)-O(2)#1	179.999(1)
O(1)#1-Ir(1)-C(6)#1	90.7(2)
O(1)-Ir(1)-C(6)#1	89.3(2)
O(2)-Ir(1)-C(6)#1	89.9(2)
O(2)#1-Ir(1)-C(6)#1	90.1(2)
O(1)#1-Ir(1)-N(1)#1	90.7(2)
O(1)-Ir(1)-N(1)#1	89.3(2)
O(2)-Ir(1)-N(1)#1	89.9(2)
O(2)#1-Ir(1)-N(1)#1	90.1(2)
C(6)#1-Ir(1)-N(1)#1	0.0(4)
O(1)#1-Ir(1)-N(1)	89.3(2)
O(1)-Ir(1)-N(1)	90.7(2)
O(2)-Ir(1)-N(1)	90.1(2)
O(2)#1-Ir(1)-N(1)	89.9(2)
C(6)#1-Ir(1)-N(1)	180.000(1)
N(1)#1-Ir(1)-N(1)	180.000(1)
C(4)-O(2)-Ir(1)	120.7(4)
C(2)-O(1)-Ir(1)	121.7(4)
C(11)-N(1)-C(7)	117.6(6)
C(11)-N(1)-Ir(1)	120.7(5)

C(7)-N(1)-Ir(1)	121.7(5)
O(1)-C(2)-C(3)	127.0(6)
O(1)-C(2)-C(1)	115.2(6)
C(3)-C(2)-C(1)	117.8(6)
C(2)-C(3)-C(4)	128.1(7)
O(2)-C(4)-C(3)	127.0(6)
O(2)-C(4)-C(5)	112.3(7)
C(3)-C(4)-C(5)	120.7(7)
N(1)-C(7)-C(8)	122.1(7)
C(9)-C(8)-C(7)	120.4(8)
C(8)-C(9)-C(10)	118.8(8)
C(11)-C(10)-C(9)	120.0(8)
N(1)-C(11)-C(10)	121.2(7)

Symmetry transformations used to generate equivalent atoms:

#1 -x,-y+1,-z+1

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for acacm (**Ph-Ir-Py**). The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ir(1)	31(1)	43(1)	31(1)	-3(1)	4(1)	-5(1)
O(2)	43(3)	33(2)	34(2)	-2(2)	11(2)	-3(2)
O(1)	36(2)	35(2)	39(2)	-7(2)	3(2)	-5(2)
N(1)	35(3)	39(3)	37(3)	2(3)	8(2)	-4(2)
C(1)	38(4)	42(4)	78(5)	-8(4)	9(4)	-11(3)
C(2)	37(3)	29(3)	54(4)	-1(3)	1(3)	-8(3)
C(3)	40(4)	52(4)	56(4)	-5(4)	16(3)	-11(3)
C(4)	48(4)	41(4)	42(4)	2(3)	10(3)	8(3)
C(5)	73(6)	92(7)	46(5)	-7(4)	25(4)	-5(5)
C(6)	35(3)	39(3)	37(3)	2(3)	8(2)	-4(2)
C(7)	46(4)	46(4)	45(4)	0(3)	4(3)	-4(3)
C(8)	53(5)	35(4)	76(6)	4(4)	14(4)	-6(3)
C(9)	72(6)	50(5)	59(5)	20(4)	14(4)	17(4)
C(10)	63(5)	78(6)	41(4)	16(4)	1(4)	10(4)

C(11)	55(4)	55(5)	34(3)	-6(3)	2(3)	6(4)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for acacm (**Ph-Ir-Py**).

	x	y	z	U(eq)
H(1A)	4464	8186	5162	79
H(1B)	5537	6858	5388	79
H(1C)	4330	7380	6182	79
H(3)	4265	6235	3704	58
H(5A)	2765	3756	2289	104
H(5B)	3637	5185	2159	104
H(5C)	1748	5019	1837	104
H(7)	523	1954	4429	55
H(8)	1797	-12	5045	65
H(9)	3301	24	6583	72
H(10)	3427	2065	7522	73
H(11)	2212	4052	6837	58

Table 1. Crystal data and structure refinement for C23 H28 Ir N O4 (**$PhCH_2CH_2$-Ir-Py**).

Identification code	iretphpm	
Empirical formula	C23 H28 Ir N O4	
Formula weight	574.66	
Temperature	153(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 8.3752(12) Å	α= 90°.
	b = 19.188(3) Å	β= 96.132(2)°.
	c = 14.088(2) Å	γ = 90°.
Volume	2251.0(6) $Å^3$	
Z	4	
Density (calculated)	1.696 Mg/m^3	

Absorption coefficient	5.959 mm^{-1}
F(000)	1128
Crystal size	0.39 x 0.04 x 0.01 mm^3
Theta range for data collection	2.12 to 27.52°.
Index ranges	-10<=h<=10, -22<=k<=24, -16<=l<=18
Reflections collected	13453
Independent reflections	5012 [R(int) = 0.0550]
Completeness to theta = 27.52°	97.0 %
Transmission factors	min/max ratio: 0.445
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5012 / 0 / 266
Goodness-of-fit on F^2	1.038
Final R indices [I>2sigma(I)]	R1 = 0.0564, wR2 = 0.1334
R indices (all data)	R1 = 0.0914, wR2 = 0.1472
Largest diff. peak and hole	3.744 and -2.422 e.$Å^{-3}$

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for C23 H28 Ir N O4 (**$PhCH_2CH_2$-Ir-Py**). U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Ir(1)	10234(1)	1251(1)	3317(1)	33(1)
O(1)	11342(9)	1313(3)	4652(5)	44(2)
O(2)	11984(8)	1756(3)	2711(5)	40(2)
O(3)	8502(7)	752(3)	3933(4)	34(1)
O(4)	9094(7)	1200(3)	1983(4)	34(1)
N(1)	11402(8)	264(4)	3113(5)	33(2)
C(1)	13170(15)	1714(7)	5919(8)	68(4)
C(2)	12639(13)	1662(6)	4853(8)	48(3)
C(3)	13546(12)	1984(5)	4190(8)	48(3)
C(4)	13208(11)	2012(5)	3204(8)	42(2)
C(5)	14395(12)	2377(5)	2647(9)	55(3)
C(6)	5942(12)	288(5)	4064(8)	51(3)
C(7)	7155(11)	624(5)	3464(7)	38(2)
C(8)	6694(11)	728(5)	2504(7)	39(2)

C(9)	7648(11)	990(5)	1822(6)	33(2)
C(10)	6908(13)	1041(6)	801(7)	49(3)
C(11)	11328(11)	-277(5)	3712(7)	38(2)
C(12)	11989(12)	-917(5)	3582(8)	45(2)
C(13)	12749(13)	-1035(6)	2773(9)	53(3)
C(14)	12841(12)	-487(5)	2147(8)	48(3)
C(15)	12188(11)	130(5)	2336(7)	40(2)
C(16)	9052(16)	2114(6)	3479(8)	69(4)
C(17)	9539(14)	2691(6)	4169(9)	67(4)
C(18)	8292(13)	3249(5)	4265(7)	45(2)
C(19)	7916(12)	3734(5)	3569(7)	48(2)
C(20)	6697(14)	4202(5)	3604(9)	55(3)
C(21)	5835(15)	4202(7)	4394(10)	69(4)
C(22)	6178(14)	3736(7)	5100(8)	61(3)
C(23)	7395(13)	3262(6)	5040(7)	50(3)

Table 3. Bond lengths [Å] and angles [°] for C23 H28 Ir N O4 (**$PhCH_2CH_2$-Ir-Py**).

Ir(1)-C(16)	1.956(13)
Ir(1)-O(1)	2.010(6)
Ir(1)-O(3)	2.011(6)
Ir(1)-O(4)	2.017(6)
Ir(1)-O(2)	2.021(6)
Ir(1)-N(1)	2.165(7)
O(1)-C(2)	1.281(12)
O(2)-C(4)	1.273(11)
O(3)-C(7)	1.269(11)
O(4)-C(9)	1.274(10)
N(1)-C(11)	1.342(11)
N(1)-C(15)	1.360(11)
C(1)-C(2)	1.523(14)
C(2)-C(3)	1.409(15)
C(3)-C(4)	1.388(14)
C(4)-C(5)	1.503(13)
C(6)-C(7)	1.532(12)

C(7)-C(8)	1.380(13)
C(8)-C(9)	1.406(12)
C(9)-C(10)	1.507(12)
C(11)-C(12)	1.368(13)
C(12)-C(13)	1.382(15)
C(13)-C(14)	1.381(14)
C(14)-C(15)	1.342(13)
C(16)-C(17)	1.500(14)
C(17)-C(18)	1.512(14)
C(18)-C(19)	1.364(14)
C(18)-C(23)	1.391(14)
C(19)-C(20)	1.364(14)
C(20)-C(21)	1.391(16)
C(21)-C(22)	1.345(17)
C(22)-C(23)	1.375(15)

C(16)-Ir(1)-O(1)	91.7(4)
C(16)-Ir(1)-O(3)	87.4(4)
O(1)-Ir(1)-O(3)	84.6(3)
C(16)-Ir(1)-O(4)	87.4(4)
O(1)-Ir(1)-O(4)	179.0(2)
O(3)-Ir(1)-O(4)	95.0(2)
C(16)-Ir(1)-O(2)	92.4(4)
O(1)-Ir(1)-O(2)	94.8(3)
O(3)-Ir(1)-O(2)	179.4(3)
O(4)-Ir(1)-O(2)	85.6(2)
C(16)-Ir(1)-N(1)	176.5(4)
O(1)-Ir(1)-N(1)	90.4(3)
O(3)-Ir(1)-N(1)	89.9(2)
O(4)-Ir(1)-N(1)	90.6(2)
O(2)-Ir(1)-N(1)	90.3(2)
C(2)-O(1)-Ir(1)	122.3(7)
C(4)-O(2)-Ir(1)	122.2(7)
C(7)-O(3)-Ir(1)	120.6(6)
C(9)-O(4)-Ir(1)	121.8(6)
C(11)-N(1)-C(15)	114.8(8)

C(11)-N(1)-Ir(1)	122.7(6)
C(15)-N(1)-Ir(1)	122.4(6)
O(1)-C(2)-C(3)	126.0(9)
O(1)-C(2)-C(1)	113.8(10)
C(3)-C(2)-C(1)	120.2(10)
C(4)-C(3)-C(2)	127.8(10)
O(2)-C(4)-C(3)	126.6(10)
O(2)-C(4)-C(5)	115.7(9)
C(3)-C(4)-C(5)	117.7(9)
O(3)-C(7)-C(8)	128.5(9)
O(3)-C(7)-C(6)	113.5(9)
C(8)-C(7)-C(6)	118.0(9)
C(7)-C(8)-C(9)	127.0(9)
O(4)-C(9)-C(8)	126.2(9)
O(4)-C(9)-C(10)	115.8(8)
C(8)-C(9)-C(10)	118.0(8)
N(1)-C(11)-C(12)	124.3(9)
C(11)-C(12)-C(13)	119.1(10)
C(12)-C(13)-C(14)	117.6(10)
C(15)-C(14)-C(13)	119.6(10)
C(14)-C(15)-N(1)	124.6(10)
C(17)-C(16)-Ir(1)	126.5(9)
C(16)-C(17)-C(18)	115.9(10)
C(19)-C(18)-C(23)	116.7(9)
C(19)-C(18)-C(17)	121.9(10)
C(23)-C(18)-C(17)	121.3(10)
C(20)-C(19)-C(18)	122.7(10)
C(19)-C(20)-C(21)	118.9(11)
C(22)-C(21)-C(20)	120.2(11)
C(21)-C(22)-C(23)	119.7(11)
C(22)-C(23)-C(18)	121.8(11)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for C23 H28 Ir N O4 (**$PhCH_2CH_2$-Ir-Py**). The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ir(1)	23(1)	41(1)	34(1)	-1(1)	-4(1)	2(1)
O(1)	43(4)	49(4)	36(4)	-2(3)	-11(3)	14(3)
O(2)	31(4)	37(3)	50(4)	7(3)	-5(3)	-6(3)
O(3)	19(3)	52(4)	30(3)	3(3)	3(2)	12(3)
O(4)	23(3)	47(4)	29(3)	2(3)	-3(2)	-3(3)
N(1)	17(4)	47(4)	34(4)	1(3)	-2(3)	-1(3)
C(1)	52(8)	97(9)	47(7)	-17(6)	-24(6)	14(7)
C(2)	34(6)	54(6)	52(7)	-12(5)	-19(5)	20(5)
C(3)	24(5)	51(6)	66(7)	-10(5)	-14(5)	7(4)
C(4)	18(5)	42(5)	65(7)	-8(5)	-3(4)	1(4)
C(5)	29(6)	42(6)	92(9)	1(6)	-3(5)	-10(4)
C(6)	35(6)	66(7)	54(7)	19(5)	17(5)	-5(5)
C(7)	30(5)	45(5)	42(6)	-5(4)	12(4)	6(4)
C(8)	21(5)	55(6)	43(6)	-2(5)	9(4)	0(4)
C(9)	20(5)	40(5)	38(5)	2(4)	-2(4)	-1(4)
C(10)	31(6)	78(7)	37(6)	-1(5)	-8(4)	-3(5)
C(11)	29(5)	47(5)	36(5)	-1(4)	-2(4)	-5(4)
C(12)	35(6)	44(5)	53(6)	-2(5)	-5(5)	-6(4)
C(13)	28(5)	49(6)	78(8)	-20(6)	-7(5)	6(4)
C(14)	28(5)	62(7)	53(6)	-20(5)	4(5)	-2(5)
C(15)	26(5)	61(6)	33(5)	0(5)	2(4)	0(5)
C(16)	81(9)	90(9)	37(6)	-22(6)	5(6)	-45(7)
C(17)	45(7)	79(8)	75(9)	-23(7)	-12(6)	18(6)
C(18)	47(6)	45(6)	43(6)	-15(5)	-3(5)	11(5)
C(19)	35(5)	63(6)	46(6)	-9(6)	15(4)	-5(5)
C(20)	49(7)	37(6)	76(8)	-3(5)	-6(6)	0(5)
C(21)	42(7)	75(8)	88(10)	-49(8)	-6(6)	22(6)
C(22)	37(6)	96(9)	49(7)	-15(7)	5(5)	2(7)
C(23)	42(6)	72(7)	36(6)	-8(5)	-2(5)	-2(6)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for C23 H28 Ir N O4 (**$PhCH_2CH_2$-Ir-Py**).

	x	y	z	U(eq)
H(1A)	13801	2140	6048	101
H(1B)	13829	1308	6123	101
H(1C)	12222	1728	6270	101
H(3)	14505	2210	4448	58
H(5A)	15415	2122	2716	82
H(5B)	14570	2853	2891	82
H(5C)	13973	2395	1971	82
H(6A)	6411	-135	4370	76
H(6B)	4965	166	3652	76
H(6C)	5676	616	4556	76
H(8)	5618	611	2281	47
H(10A)	7475	1397	467	74
H(10B)	5774	1171	788	74
H(10C)	6994	590	485	74
H(11)	10780	-210	4261	45
H(12)	11926	-1275	4042	54
H(13)	13193	-1478	2653	63
H(14)	13363	-546	1586	57
H(15)	12281	499	1896	48
H(16A)	8909	2336	2841	83
H(16B)	7968	1969	3620	83
H(17A)	10513	2916	3970	81
H(17B)	9835	2482	4806	81
H(19)	8527	3747	3039	57
H(20)	6442	4522	3096	66
H(21)	5001	4533	4436	83
H(22)	5583	3735	5637	73
H(23)	7628	2935	5542	60